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Two-Dimensional Water and Ice Layers: Neutron Diffraction Studies at 278, 263, and 20 K

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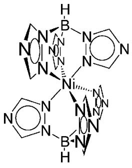
There is hardly a compound which has raised more interest than water because of its fundamental importance in many biological and chemical processes.[1] Recent investigations on water or ice include the properties of water clusters, such as $(H_2O)_n$ ($n = 3-6$),[2] the structure of water oligomers, for example, $(H_2O)_8$ or $(H_2O)_{10}$ in supramolecular crystals,[3] low-dimensional water polymers in supramolecular solids,[4] different liquid water phases,[5] molecular dynamics simulations of water freezing,[6] of water/ice in hydrophobic nanopores,[7] of hydrogen bonding and dynamics in bulk liquid water.[8] Despite a myriad of studies water is still not a fully understood liquid. Here we report a neutron diffraction study of the molecular structure of water and ice confined in an organic slit-shaped nanospace. The two-dimensional (2D) ice layers show the existence of new ice phases with chain segments or eight-membered and condensed twelve-membered rings. Such phases have not been seen before in bulk or other low-dimensional ice. Hitherto experimental[9] and theoretical[10] studies on 2D ice suggested mostly a hexagonal honeycomb lattice. Experimental studies on 2D ice usually report a structure at a single temperature, whereas here the temperature range from 2D water at 278 K down to 20 K is covered, showing the liquid−solid and a solid−solid-phase transition.

A 2D layer of water molecules is stabilized between organic layers of the nickel(II) chelate complexes **1**. The supramolecular layer clathrate structure has a slit-width for the water layer of about 3 Å (0.3 nm). Large blocky crystals with dimensions of 4 × 3 × 2 mm^3 were grown from the reaction mixture of $NiCl_2$ and potassium-tris(triazolyl)borate in D_2O or H_2O.[11] Single-crystal neutron structure investigations were carried out at 278, 263, and 20 K with a D_2O-containing crystal.[12,13]



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For each measuring temperature a different space group is found. The symmetry of the orthorhombic cell decreases from *c*-centered (*Cmca*) at 278 K[14] via centrosymmetric primitive (*Pmnb*) at 263 K[15] to acentric primitive ($P2_1nb$) at 20 K.[16] Some reflection intensities were recorded during the cooling and warming of the crystal (Figure 1). The abrupt change in intensity for the 3 0 1 reflection at 277 K is indicative of a phase transition. Going from *Cmca* to *Pmnb* is a klassengleich (class-equal) transition of type 2 (k2); from *Pmnb* to $P2_1nb$ it is a translationsgleich (translation-equal) transition of type 2 (t2). The phase transition from *Pmnb* to $P2_1nb$ involves the loss of the inversion symmetry element and leads to merohedral twinning.[17]

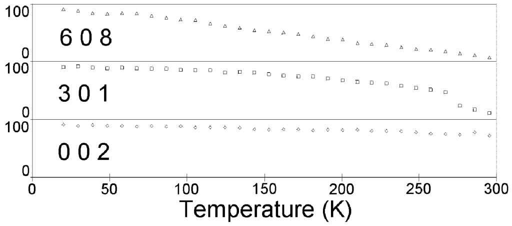

Figure 1. Relative changes in intensity of selected reflections upon warming of a crystal of **1**·$6D_2O$ on the neutron diffactometer.

The first phase transition upon cooling occurs close to the freezing point of H_2O (273.15 K, 0 °C) or D_2O (276.95 K, 3.8 °C) and was shown by differential scanning calorimetry to be at −0.3 °C for **1**·$6H_2O$ and at +3.1 °C for **1**·$6D_2O$.[18] The change in space group, that is, the loss of symmetry elements with decreasing temperature is solely due to an ordering phenomenon in the 2D water substructure as will be discussed in the following.

At 278 K (5 °C) and above, the water molecules in **1**·$6D_2O$ exhibit pronounced disorder (Figure 2a) and interact only weakly with the surrounding layers of the complex molecules. Of the six molecules per formula unit four are disordered. The remaining two are H/D-bonded to the N atoms of the surrounding organic complex molecules. The disorder is indicative of the expected thermal mobility and dynamic nature of liquid water. The neutron diffraction experiment shows a time-averaged picture of the water structure. Each of four disordered D_2O molecules appears spread over three positions. At any given time only one of these positions will be occupied. Some of the O atom positions are within hydrogen-bonding distance of each other. Taking an O···O separation of 2.6−3.0 Å for hydrogen bonding, the 2D water layer can then be seen as being built-up from different, small D_2O clusters containing 2−6 molecules and free D_2O molecules.

Liquid 3D water can be modeled as a mixture of H_2O clusters of different sizes and single H_2O molecules between the clusters. In the center of the cluster the H_2O molecules are four-fold coordinated by H-bonds. At the cluster surface the H_2O molecules are involved in only one to three H-bonds. This leads to a dynamic increase or reduction of the cluster sizes.[19] Thus, we see the water layer in **1**·$6D_2O$ at 278 K as close to a 2D liquid phase. This is further supported by the observed loss of water from the crystal within minutes when the crystal is taken to an atmosphere not saturated with water vapor. When localized H-bonds exist to each water molecule such fast water loss is seldom observed, and there is also less disorder.

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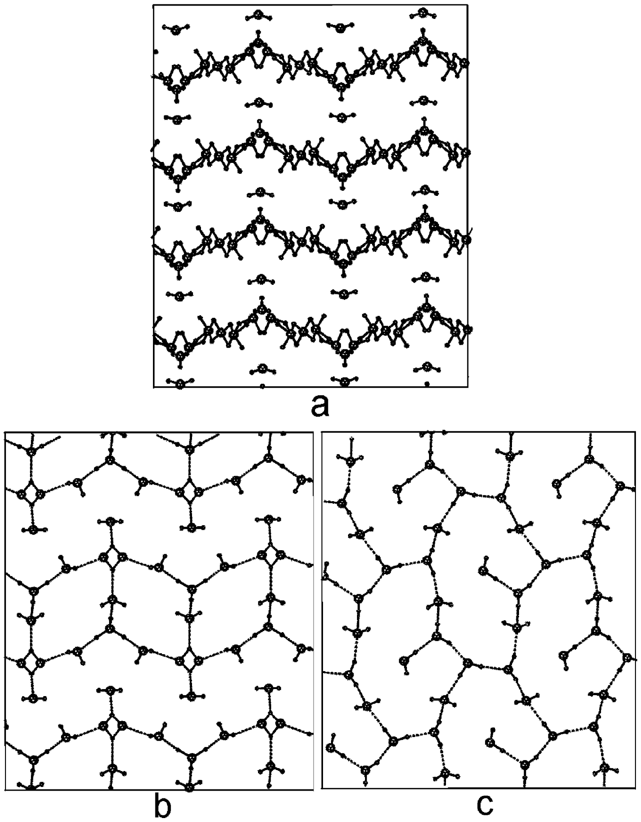

Figure 2. Two-dimensional infinite water/ice layers in **1**·6D_2O from a neutron diffraction study at (a) 278 K, (b) 263 K, and (c) 20 K.

Cooling of the crystal through the phase transition at 276 K leads to a strong increase in order, that is, freezing within the water layer. At 263 K observation of the individual hydrogen bonds becomes possible (Figure 2b). The water molecules are organized in kinked strands composed of rings of eight water molecules. But within the strands one O and a D atom are crystallographically disordered over two positions. Considering only one of these positions as fully occupied, the strands are disrupted, giving either individual rings of eight molecules or folded-chain segments. The interaction with the organic environment increases slightly with now two more D_2O molecules (per formula unit) entering into an, albeit very weak, hydrogen-bonded contact to a nitrogen atom.

At 20 K a fully localized water structure is found. There is no more disorder. All D atoms form typical hydrogen bonds to other water molecules or to nitrogen atoms of the complex molecules (Figure 2c). The water layer is an infinite 2D net of O_{12} rings with a dangling D_2O molecule. Both low-temperature structures feature water molecules which are surrounded by two or three other water molecules. One water molecule has only one D_2O neighbor.

Neutron diffraction studies have shown the stepwise freezing of a dynamic layer of pseudoliquid 2D water. The role of the complex molecules **1** is to provide the geometric constraints for the two-dimensionality of the water layer substructure; some H-bonding contacts to the surrounding organic complex molecules are unavoidable. The structure of 2D ice layers features novel rings of eight water molecules or folded-chain segments at temperatures below the freezing point. At very low temperature an unprecedented net of condensed irregular rings of 12 water molecules (plus a dangling D_2O) is observed. Both ice layers are different from hitherto known 2D ice phases which mostly consist of hexagonal honeycomb lattices.[9,10] Our 2D ice layers do not satisfy the conventional Bernal−Fowler "ice rules";[20] hence, they cannot be stand-alone solid phases in a vacuum at low temperatures. Ice at and near the surface, however, has unique properties and reduced order parameters and is not in a Bernal−Fowler state due to the specific boundary conditions on the ice surface.[21]

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Supporting Information Available: Crystallographic files for the structures of 1·6D_2O at 278, 263 and 20 K (CIF). Figures with details of the water layer at 263 and 20 K, table with hydrogen bond distances and angles at 263 and 20 K (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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(15) Orthorhombic, *Pmnb*, nonstandard setting of *Pnma*, $a = 10.852(2)$ Å, $b = 20.919(3)$ Å, $c = 11.696(1)$ Å, $V = 2655.0(6)$ $Å^3$, $Z = 4$, $D_c = 1.563$ g·cm^{-3}, R, R_w 0.0503, 0.1132 for 2048 independent reflections with $I > 2\sigma(I)$.
(16) Orthorhombic, $P2_1nb$, nonstandard setting of $Pna2_1$, $a = 10.755(1)$ Å, $b = 20.736(2)$ Å, $c = 11.587(2)$ Å, $V = 2584.0(5)$ $Å^3$, $Z = 4$, $D_c = 1.570$ g·cm^{-3}, R, R_w 0.0285, 0.0667 for 2881 independent reflections with $I > 2\sigma(I)$.
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